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# PATENT SPECIFICATION

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NO DRAWINGS

(21) Application No. 20001/68 (22) Filed 26 April 1968
(31) Convention Application No. 634074 (32) Filed 27 April 1967 in
(33) United States of America (US)
(45) Complete Specification published 6 Jan. 1971
(51) International Classification C 07 d 51/36 A 01 n 9/12 9/22
(52) Index at acceptance

C2C 171—27X—289 1E4K4 1E5K4 1G5B 1G6A2 1G6A3 1G6B5 1G6B6 1Q11J 1Q1B 1Q4 1Q6C 1Q7A 1Q7B 1Q8A 1Q9F2 215 220 226 22Y 246 250 252 25Y 30Y 321 322 326 32Y 332 342 345 34Y 360 363 36Y 3A13A1A4 3A13A1L 3A13A3A4 3A13A3B3 3A13A3F3 3A13A3K 3A13C10A 3A13C10D 3A13C10H 3A13C1C 3A13C2C 3A13C9 43X 456 45Y 509 50Y 579 5A4 5E2 601 619 620 621 62X 62Y 650 652 656 660 661 681 699 701 709 719 73Y 774 777 778 791 79Y B4A1 KG MM MV NJ NL NS

A5E 1C17 1C4B2 1C4B3 1C4B4

C1B 3F1

(72) Inventors JAMES DAVID DAVENPORT
RONALD ERVIN HACKLER and

PATENTS ACT 1949

SPECIFICATION NO. 1,218,623

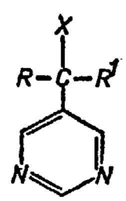
The following amendments were allowed under Section 29 on 2 June 1971:-

Page 1, lines 25 and 47, page 5, lines 96 and 97, page 10, line 19, *delete* comma *insert* 'and' *after* 'X' *delete* 'and the pyrimidine ring'

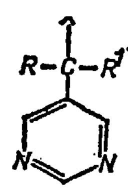
Page 5, line 83, *after* 'thienyl' *delete* comma *insert* 'and'

Page 5, line 84, *delete* 'and pyrimidine'

THE PATENT OFFICE
*1 July 1971*



wherein
R is $C_1$—$C_{13}$ alkyl, $C_3$—$C_8$ cycloalkyl, or phenyl;
$R^1$ is benzyl, phenyl, thienyl, or furyl, $C_1$—$C_{13}$ alkyl, or $C_3$—$C_8$ cycloalkyl;
X is hydrogen, hydroxyl, $C_1$—$C_4$ acyloxy, halo, amino, cyano, ($C_1$—$C_4$ acyl) amino, halo, amino, cyano, ($C_1$—$C_4$ acyl) amino, $C_1$—$C_3$ alkyl, $C_1$—$C_3$ alkoxy, $C_1$—$C_3$ alkylmercapto, anilino, heterocyclic-mercapto, or hydroxylamino; and where-



wherein
R is $C_1$—$C_{13}$ alkyl, $C_3$—$C_8$ cycloalky phenyl;
$R^1$ is benzyl, phenyl, thienyl, or furyl, $C_{13}$ alkyl, or $C_3$—$C_8$ cycloalkyl;
X is rydrogen, hydroxyl, $C_1$—$C_4$ acy halo, amino, cyano, ($C_1$—$C_4$ acyl) ar $C_1$—$C_3$ alkyl, $C_1$—$C_3$ alkoxy, $C_1$ alkylmercapto, anilino, heteroc mercapto, or hydroxylamino; and w in the R, $R^1$, X and the pyrimidine

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A5E 1C17 1C4B2 1C4B3 1C4B4

C1B 3F1

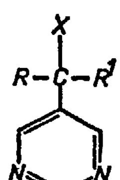


(72) Inventors JAMES DAVID DAVENPORT
RONALD ERVIN HACKLER and
HAROLD MELLON TAYLOR

## (54) SUBSTITUTED-5-PYRIMIDINE COMPOUNDS

(71) We, ELI LILLY AND COMPANY, a Corporation of the State of Indiana, United States of America, of 740 South Alabama Street, City of Indianapolis, State of Indiana, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to substituted 5-pyrimidine compounds of the formula:



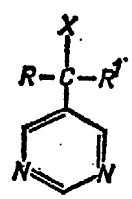
wherein

R is $C_1$—$C_{13}$ alkyl, $C_3$—$C_8$ cycloalkyl, or phenyl;

$R^1$ is benzyl, phenyl, thienyl, or furyl, $C_1$—$C_{13}$ alkyl, or $C_3$—$C_8$ cycloalkyl;

X is hydrogen, hydroxyl, $C_1$—$C_4$ acyloxy, halo, amino, cyano, ($C_1$—$C_4$ acyl) amino, halo, amino, cyano, ($C_1$—$C_4$ acyl) amino, $C_1$—$C_3$ alkyl, $C_1$—$C_3$ alkoxy, $C_1$—$C_3$ alkylmercapto, anilino, heterocyclic-mercapto, or hydroxylamino; and wherein R, $R^1$, X and the pyrimidine ring may be substituted by one or more of the radicals, chloro, bromo, fluoro, iodo, trifluoromethyl, hydroxy, methyl, ethyl, methoxy, methylmercapto, methylsulfonyl, nitro or dialkylamino; the non-phytotoxic acid addition salts formable therewith; and excluding 5-isopropylpyrimidine and 5-isoheptylpyrimidine.

A process for the preparation of the pyrimidine compounds of the formula:



wherein

R is $C_1$—$C_{13}$ alkyl, $C_3$—$C_8$ cycloalkyl, or phenyl;

$R^1$ is benzyl, phenyl, thienyl, or furyl, $C_1$—$C_{13}$ alkyl, or $C_3$—$C_8$ cycloalkyl;

X is rydrogen, hydroxyl, $C_1$—$C_4$ acyloxy, halo, amino, cyano, ($C_1$—$C_4$ acyl) amino, $C_1$—$C_3$ alkyl, $C_1$—$C_3$ alkoxy, $C_1$—$C_3$ alkylmercapto, anilino, heterocyclic-mercapto, or hydroxylamino; and wherein the R, $R^1$, X and the pyrimidine ring

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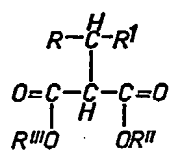
may be substituted by one or more of the radicals chloro, bromo, fluoro, iodo, trifluoromethyl, hydroxy, methyl, ethyl, methoxy, methylmercapto, methylsulfonyl, nitro or dialkylamino; the nonphytotoxic acid addition salts formable therewith; and excluding 5-isopropylpyrimidine and 5-isoheptylpyrimidine comprises:

(A) when X is a hydroxyl group, reacting a 5-halopyrimidine, a ketone of the formula R—C:O—$R^1$ wherein R and $R^1$ are as defined above, and an alkyl alkali metal in the cold in the presence of a low-melting polar organic solvent or mixture of solvents;

(B) when X is a hydrogen atom, reacting

(1) a substituted malonic acid ester of the formula



wherein R and $R^1$ are as defined above and R'' and R''' are $C_1$—$C_4$ alkyl radicals, with urea or an appropriately substituted derivative thereof, reacting the barbituric acid derivative thus obtained with phosphorus oxyhalide, and hydrogenating the result-trihalo-pyrimidine derivative thus obtained; or

(2) an alcohol produced in accordance with step (A) above with a reducing agent to replace the hydroxy group with a hydrogen atom;

(C) when X is a cyano group, reacting a 5-halopyrimidine with a compound of the formula

$$\begin{array}{c} H \\ | \\ R\text{—}C\text{—}R^1 \\ | \\ CN \end{array}$$

wherein R and R' are as defined above, in the presence of a solvent and an alkali metal amide;

(D) when X is a halogen atom, reacting an alcohol produced in accordance with step (A) with a halogenating agent to replace the hydroxyl group of the alcohol with the corresponding halogen atom;

(E) when X is $C_1$—$C_3$ alkoxy, reacting a 5 - $\alpha$ - halopyrimidine produced in accordance with step (D) above with the corresponding alkali metal alkoxide in alkanol solution;

(F) when X is an amino group, reacting a 5 - $\alpha$ - halopyrimidine produced in accordance with step (D) above with liquid ammonia at an elevated temperature and pressure;

(G) when X is a hydroxylamino group, reacting a 5 - $\alpha$ - halopyrimidine produced in accordance with step (D) above with hydroxylamine in the presence of an alkali metal alkoxide and an alkanol;

(H) when X is an anilino group, reacting a 5 - $\alpha$ - halopyrimidine produced in accordance with step (D) above with aniline in the presence of an inert solvent at an elevated tempertuare;

(I) when X is a $C_1$—$C_3$ alkylmercapto or heterocyclomercapto group, reacting the corresponding mercaptan with a 5 - $\alpha$ - halopyrimidine produced in accordance with step (D) above in the presence of a base and an inert solvent;

(J) when X is $C_1$—$C_4$ acyloxy or $C_1$—$C_4$ acylamino, reacting an alcohol produced in accordance with step (A) above or an amine produced in accordance with step (F) above, respectively, with the corresponding $C_1$—$C_4$ alkanoic acid or reactive derivative thereof;

and optionally reacting the product obtained by any of said steps with an acid selected to provide a nonphytotoxic salt thereof.

$C_1$—$C_3$ Alkyl means methyl, ethyl, *n*-propyl or iso-propyl.

Lower acyl means formyl, acetyl, propionyl, or butyryl.

$C_1$—$C_{13}$ Alkyl means saturated straight or branched chain aliphatic hydrocarbon radicals and can be illustratively methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec.*-butyl, *tert.*-butyl, *n*-amyl, isoamyl, *sec.*-amyl, tertiary amyl and other isomeric amyl, *n*-hexyl, isohexyl, *sec.*-hexyl, and other isomeric hexyl, *n*-heptyl, and other isomeric heptyls, *n*-octyl, isooctyl, and other isomeric octyls, *n*-primary nonyl (nonyl-1), nonyl-2, nonyl-3, nonyl-5, 2 - methyloctyl - 2, 4 - ethyl - heptyl - 4, 3 - methyl - 4 - ethyl - hexyl -4,3 - methyl - 3 - ethyl - pentyl - 3, 2 -ethyl - hexyl - 1, *n*-primary decyl (decyl-1), decyl-4, 2 - ethyl - octyl - 3 (tertiary decyl), undecyl, *n*-dodecyl and *n*-tridecyl.

$C_1$—$C_3$ Alkoxy means methoxy, ethoxy, propoxy, or isopropoxy.

$C_1$—$C_3$ Alkylmercapto means methylmercapto, ethylmercapto, *n*-propylmercapto, or isopropylmercapto.

Heterocyclic mercapto means e.g. imid-

azolylmercapto, furylmercapto and thienylmercapto.

Halo means bromo, chloro, fluoro, or iodo.

$C_3$—$C_8$ Cycloalkyl means saturated monocyclic aliphatic hydrocarbon rdaicals having three to eight carbon atoms in the ring and can be illustratively cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl.

Suitable nonphytotoxic acid addition salts of the bases represented by the above formula can be prepared employing those acids of sufficient acidity to form acid addition salts with the weakly basic pyrimidine group or with an amine substituent attached thereto. These include, *inter alia,* hydrobromic, sulfuric, phosphoric, nitric, oxalic, methanesulfonic, hydrochloric, hydroiodic, benzenesulfonic, *p*-toluenesulfonic, maleic and the like.

In the prior art, Margot et al., U.S. Patent 2,839,446 (June 17, 1958), teach novel pyrimidines which are said to possess fungicidal activity. The Margot compounds are distinguished by having at least one trichloromethane sulphenylmercapto group preferably attached at the 2-position of the pyrimidine ring.

In addition, Ballard et al., U.S. Patent 2,658,895 (November 10, 1953), teach 2 - alkylphenyl - 3,4,5,6 - tetrahydro - pyrimidines which are said to have fungicidal and detergent properties and also to have use as asphalt additives.

Brederick et al., Chem. Ber., 93, 230—35 (1960), teach the preparation of 5-isopropylpyrimidine and 5-isoheptylpyrimidine, respectively. No utility is disclosed therefor.

Lowin et al., Arch. Biochem. and Biophysics, 101, 197—203 (1963), teach the use of 5-hydroxymethylpyrimdine as a substrate in studying the *in vivo* inhibition of thiamine synthesis.

The novel pyrimidines of the present invention have been found useful in controlling fungi which attack food crops, ornamental plants, and turf. The novel compounds have been found useful in combatting both airborne and soil-borne fungi which affect plants. Most unexpectedly and surprisingly, the novel pyrimidine compounds of this invention, unlike the closely related pyridine compounds, are systemaically active as fungicidal agents. That is, the pyrimidine compounds are absorbed by the plant and transported throughout the plant via the vascular system of the plant. Further, these novel pyrimidines have the ability to cause certain plants to produce, in a manner as yet not known or understood, fungicidal substances of an unknown structure which substances can be extracted from the plant tissues by methods known to the art and shown to possess fungicidal activity in standard fungicidal tests.

The systemic antifungal action of these pyrimidines has been demonstrated by the following remarkable experiment: Seeds of cucumber, for example, are soaked for a short period of time, about 10 minutes, in an ethanol-light isoparaffin oil solution of a 5-substituted pyrimidine. The seeds are removed, dried, and planted, and produce plants free from powder mildew and protected therefrom.

The novel compounds of the present invention have been shown by suitable *in vitro* and *in vivo* tests to control such fungi as *Erysiphe polygoni,* the causative organism of bean powdery mildew; *Colletotrichum lagenarium,* the causative organism of cucumber anthracnose; *Uromyces phaseoli,* the causative organism of bean rust; *Piricularis oryzae,* the causative organism of rice blast; and *Rhizoctonia solani,* the causative organism of damping-off in cotton.

In addition, certain fungi which affect ornamental plants including *Sphaerotheca pannosa* var. *rosae,* the causative organism of powdery mildew of rose; and *Erysiphe graminis,* the causative organism of powdery mildew of turf are controlled by the novel pyrimidines of this invention.

The novel compounds of this invention are also active against certain turf pathogens which yearly inflict great damage to turf. These turf pathogens include *Helminthosporium sativum,* the causative organism of Leaf Spot; *Rhizoctonia solani,* the causative organism of Brown Patch; *Sclerotinia homoeocarpa,* the causative organism of Dollar Spot; *Fusarium roseum,* the causative organism of Root Rot; and *Pythium sp.,* the causative organism of Pythium Blight.

The novel compounds of this invention are utilized as fungicides by applying them to infected or susceptible plant surfaces, or to the soil. This is conveniently accomplished by spraying, dipping, dusting, or drenching.

For such use, the compounds are formulated into compositions desirably containing, in addition to the 5-substituted pyrimidine, one or more of a plurality of additaments including water, polyhydroxy compounds, petroleum distillates, and other dispersion media, surface-active dispersing agents, emulsifiers, and finely divided inert solids. The concentration of the 5-substituted pyrimidine compound in these compositions may vary depending on whether the composition is intended as an emulsifiable concentrate or a wettable powder designed to be subsequently diluted with additional inert carrier such as water to produce the ultimate treating composition or is intended for direct application as a dust to plants.

The novel compounds of the present invention are applied to plants in effective amounts, varying somewhat with the particular organism, with the severity of the infection, and with other factors such as the environ-

ment in which treatment is conducted. In general, it is found that an aqueous spray containing from about 2 to about 400 ppm. of active material is satisfactory when treatment is to be carried out in the greenhouse.

As is well understood in the art, a somewhat higher concentration of the active compound is desirable when treatment is to be carried out in the field. In that case, the preferred range is from about 15 to about 1000 ppm. of 5-substituted pyrimidine.

In the case of the turf pathogens, *supra*, control has been accomplished using an application rate of from about 0.05 to about 1.0 pound per acre of the 5-substituted pyrimidine. Control of the other soil-borne fungi mentioned above has been accomplished using a broadcast application rate of about 5 to 40 pounds per acre of the 5-substituted pyrimidines.

Unexpected antibacterial activity has been shown by certain of the novel compounds. Thus, $\alpha$,$\alpha$ - diphenyl - 5 - pyrimidinemethanol and 2 - methyl - 5 - diphenylmethyl - 4,6 - pyrimidinediol, are active against *Agrobaoterium tumefaciens,* the causative organism of crown gall. Other of the novel compounds, including 2,4,6 - trichloro - 5 - diphenylmethylpyrimidine, 5 - (2 - chlorodiphenylmethyl)pyrimidine, 2 - chloro - 5 - diphenylmethylpyrimidine, and 5 - bis(4 - chlorophenyl)methylpyrimidine are active against *Xanthomonas phaseoli* var. *sojensis*, the causative organism of bacterial blight of soybean.

Besides the above properties, the novel pyrimidines have shown unexpected herbicidal activity. In addition, the compounds possess interesting growth-inhibitor activity. Thus, 5 - (2 - chlorodiphenylmethyl)pyrimidine has bene shown to inhibit tobacco sucker growth.

Another of the novel compounds, $\alpha$ - (2 - fluorophenyl) - $\alpha$ - (3 - fluorophenyl) - 5 - pyrimidinemethanol, possesses the ability to inhibit the opening of the buds of cut flowers.

Still others of the compounds, for example, $\alpha$,$\alpha$ - diphenyl - 5 - pyrimidinemethanol and $\alpha$ - (2 - chlorophenyl) - $\alpha$ - (4 - chlorophenyl) - 5 - pyrimidinemethanol, exhibit anti-auxin properties.

Certain of the novel pyrimidines, i.e. $\alpha$ - (2 - fluorophenyl) - $\alpha$ - (3 - fluorophenyl) - 5 - pyrimidinemethanol and $\alpha$ - (2 - chlorophenyl) - $\alpha$ - (4 - chlorophenyl) - 5 - pyrimidine methanol, possess the completely unexpected and as yet unexplained ability to cause an increase in the number of flowers and fruit produced by tomato plants when said plants are treated with one of the compounds about 6 to 8 weeks prior to flower formation.

Because of the herbicidal activity of the pyrimidine compounds they are useful in fertiliser composition with one or more plant foods.

The novel 5-substituted pyrimidinemethanols (X=OH in the generic formula, *supra*) are readily prepared in good yields by a synthesis exemplified as follows: A suitable ketone, for example, benzoylcyclohexane, is dissolved in a solvent composed of equal volumes of tetrahydrofuran and ethyl ether, the solution is cooled to $-125°$C., and while maintained at that temperature, a solution of 5-bromopyrimidine in equal volumes of tetrahydrofuran and ethyl ether is added thereto. While the mixture is maintained at about $-125°$C., a hexane solution of *n*-butyl lithium is added. The reaction mixture is stirred overnight in the cold, the reaction product mixture washed successively with dilute aqueous ammonium chloride solution and water, and the organic layer separated and dried over a suitable drying agent. The dried organic layer is concentrated to dryness *in* vacuo and the solid residue extracted with ether to remove undesired by-products. The ether-insoluble material remaining is identified by the elemental analysis as $\alpha$ - cyclohexyl - $\alpha$ - phenyl - 5 - pyrimidinemethanol.

An alternative method appears preferable in some instances and proceeds as follows: In a suitable reaction flask, dry ether is maintained in an atmosphere of dry nitrogen, cooled to about $-118°$C., and a solution of butyl lithium in hexane added, followed by a solution of 5 - bromopyrimidine in tetrabutyl lithium in hexane added, followed by hydrofuran. The reaction mixture is cooled to about $-125°$C. and a solution of a suitable ketone, for example, 4 - fluorobenzophenone, in tetrahydrofuran is added at such a rate as to maintain the temperature of the reaction mixture at about $-120°$C. The reaction product mixture is stirred overnight and warmed gradually to room temperature. The mixture is neutralized with saturated aqueous ammonium chloride solution and extracted with ether. The combined ether extracts are dried, concentrated to dryness *in vacuo* and the residual material dissolved in benzene and chromatographed over a silica gel column, eluting with a mixture of ethyl acetate-benzene. The product obtained from the fraction eluted with 30:50 ethyl acetate-benzene was recrystallized from a solvent such as ether and identified as $\alpha$ - (4 - fluorophenyl) - $\alpha$ - phenyl - 5 - pyrimidinemethanol.

When X=H in the generic formula, *supra*some of the novel compounds can be prepared by heating the 5-substituted pyrimidinemethanol (prepared as above) in a mixture of glacial acetic acid and 47 percent aqueous hydriodic acid to reduce the hydroxyl group and yield the 5-substituted pyrimidinemethane.

In other compounds where X=H, the pre-

paration is accomplished by the reaction of a suitably substituted malonic ester with urea or acetamine. For example: A mixture of diethyl phenyl - p - tolylmethyl malonate and urea is allowed to react in an anhydrous alcohol such as methanol in the presence of sodium methylate to yield 2,4,6 - dihydroxy - 5 - phenyl - *p* - tolylmethylpyrimidine. This trihydroxy compound is allowed to react with excess phosphorus oxychloride to yield 2,4,6 - trichloro - 5 - phenyl - *p* - tolylmethylpyrimidine. The trichloropyrimidine is then hydrogenated in the presence of triethylamine and palladinized charcoal to yield 5 - phenyl - *p* - tolylmethylpyrimidine.

Where X=cyano in the above generic formula, the novel compounds can be prepared in the following manner: A mixture of diphenylacetonitrile and 5-bromopyrimidine is allowed to react in the presence of potassium amide in a suitable solvent such as xylene to yield $\alpha,\alpha$ - diphenyl - 5 - pyrimidine - acetonitrile.

Those compounds where $X=C_1$—$C_3$ alkoxy are prepared by allowing an alkali-metal low alkoxide such as sodium methoxide, potassium ethoxide, or sodium propoxide to react in alkanol solution with a 5-halo analogue of the desired product [e.g., 5 - ($\alpha$ - chlorodiphenylmethyl)pyrimidine] to yield the desired product [e.g., 5 - ($\alpha$ - $C_1$—$C_3$ alkoxydiphenylmethyl)pyrimidine].

Where X=amino, the compounds are prepared by heating a mixture of the analogous halo-substituted pyrimidine, such as 5 - ($\alpha$ - chlorodiphenylmethyl)pyrimidine, and excess liquid ammonia at an elevated temperature of about 100°C. in a sealed stainless-steel reaction vessel for a time sufficient to complete the reaction. The product can be isolated as the free base 5 - ($\alpha$ - aminodiphenylmethyl)pyrimidine, or in the form of a salt such as the hydrochloride, hydrobromide, or the like.

Correspondingly, 5 - ($\alpha$ - hydroxylaminodiphenylmethyl)pyrimidine and related compounds are readily prepared by allowing hydroxylamine to react with 5 - ($\alpha$ - chlorodiphenylmethyl)pyrimidine or analogous 5 - $\alpha$ - halo compounds.

Following the same general procedure, the 5 - [$\alpha$ - (2 - imidazolylthio)diphenylmethyl]-pyrimidine is readily synthesized by allowing 2 - mercaptoimidazole to react with $\alpha$ - chloro - 5 - diphenylmethylpyrimidine in the presence of a base such as sodium or potassium ethoxide in a suitable solvent such as absorlute ethanol. The reaction product mixture is concentrated to dryness at reduced pressure and the solid residue slurred or extracted with a solvent such as hot benzene to dissolve the product, 5 - [$\alpha$ - (2 - imidazolylthio)diphenylmethyl]pyrimidine, which then crystallizes from the benzene.

Where X=anilino, the compounds are readily prepared by heating a 5-halo analogue such as 5 - ($\alpha$ - chlorodiphenylmethyl)pyrimidine with aniline in an inert solvent such as benzene on the steam bath for a time sufficient to complete the reaction. The aniline hydrochloride which precipitates is filtered off, the filtrate concentrated *in vacuo* to dryness, and the residue recrystallized from a suitable solvent such as ethyl ether to yield 5 - ($\alpha,\alpha$ - diphenyl - $\alpha$ - anilinomethyl)-pyrimidine.

While the compounds of the present invention have been defined in terms of a structural formula which depicts the novel structural features of the claimed compounds and which indicates the presence therein of certain well-known organic radicals including phenyl, alkyl, furyl, thienyl, cycloalkyl, and pyrimidine, it will be recognized by those skilled in the art that such radicals may bear one or more substituents without altering the properties of the novel compounds in such a way as would set them apart from the invention or take them outside its scope. Compounds having the novel structure of the preesnt invention and bearing such substituents are accordingly to be considered as equivalents of the unsubstituted compounds and are to be considered to lie within the scope of the invention. Among such substituent atoms and radicals for R, $R^1$, X and the pyrimidine ring of the above formula are chloro, bromo, fluoro, iodo, trifluoromethyl, hydroxy, methyl, ethyl, methoxy, methylmercapto, methylsulfonyl, nitro, and dialkylamino.

The following examples describe in detail the methods used in preparing the novel compounds of this invention. In the following examples parts and percentages are by weight unless otherwise specified.

### Example 1

$\alpha$ - Cyclohexyl - $\alpha$ - phenyl - 5 - pyrimidinemethanol

To a solution of 0.1 mole of benzoylcyclohexane in 250 ml. of a mixture of equal volumes of tetrahydrofuran and ether and cooled to −125°C. was added a solution of 0.1 mole of 5 - bromopyrimidine in the same mixed solvent. The mixture was stirred and maintained at about −125°C. in a cooling bath composed of liquid nitrogen and ethanol, and to the cooled solution were added 60 ml. of a 15 percent solution of n-butyl lithium in n-hexane, and the reaction mixture was stirred overnight.

The reaction product mixture was washed successively with 10 percent aqueous ammonium chloride solution and water and dried over anhydrous potassium carbonate. The dried or organic solution was evaporated to dryness to yield a solid weighing about 14 g. The solid was extracted with ether and the undissolved solid washed twice with ether. The ether-in-soluble material was iden-

tified as α - cyclohexyl - α - phenyl - 5 - pyrimidinemethanol having a melting point of about 156—157°C.

Following the general procedure of Example 1, with appropriate starting materials, the following compounds were prepared and isolated as free bases or acid addition salts thereof:

α,α - Bis(4 - chlorophenyl) - 5 - pyrimidine methanol. Melting point: Glass.

α - Phenyl - α - (4 - chlorophenyl) - 5 - pyrimidinemethanol hydrochloride. Melting point: Glass.

α,α - Bis(cyclohexyl) - 5 - pyrimidinemethanol. Melting point: 142—144°C.

α,α - Bis(*n* - hexyl) - 5 - pyrimidinemethanol. Melting point: Viscous liquid.

α - Cyclobutyl - α - phenyl - 5 - pyrimidinemethanol. Melting point: 115—117°C.

α - Methyl - α - phenyl - 5 - pyrimidinemethanol. Melting point: 70°C.

α,α - Bis(3 - fluorophenyl) - 5 - pyrimidinemethanol. Melting point: Glass.

α - (2 - Chlorophenyl) - α - (3 - chlorophenyl) - 5 - pyrimidinemethanol. Melting point: Amorphous.

α,α - Diphenyl - 5 - pyrimidinemethanol. Melting Point: 167—170°C.

α - (2 - Chlorophenyl) - α - phenyl - 5 - pyrimidinemethanol. Melting point: 154—156°C.

α - (*n* - Pentyl) - α - phenyl - 5 - pyrimidinemethanol. Melting point: Liquid.

α - (2 - Fluorophenyl) - α - phenyl - 5 - pyrimidinemethanol. Melting point: 139—141°C.

α,α - Bis (3,4 - Dichlorophenyl) - 5 - pyrimidinemethanol hemi-etherate. Melting point: 88—89°C.

α - (Phenyl) - α - (2 - thienyl) - 5 - pyrimidinemethanol. Melting point: 140—142°C.

α,α - Bis(isopropyl) - 5 - pyrimidinemethanol. Melting point: 115—118°C.

α - (3,4 - Dichlorophenyl) - α - phenyl - 5 - pyrimidinemethanol. Melting point: Amorphous.

α - (2,4 - Dichlorophenyl) - α - phenyl - 5 - pyrimidinemethanol. Melting point: Viscous liquid.

α - (4 - Nitrophenyl) - α - phenyl - 5 - pyrimidinemethanol. Melting Point: Amorphous.

α - (2 - Fluorophenyl) - α - (3 - fluorophenyl) - 5 - pyrimidinemethanol. Melting point: 104—108°C.

α,α - Bis(*p* - tolyl) - 5 - pyrimidinemethanol. Melting point: Amorphous.

α - (2,4 - Dimethylphenyl) - α - phenyl - 5 - pyrimidinemethanol. Melting point: Amorphous.

α - Phenyl - α - (*p* - anisyl) - 5 - pyrimidinemethanol. Melting point: 95—97° C.

α - Phenyl - α - (4 - trifluoromethylphenyl - 5 - pyrimidinemethanol. Melting point: 125—127°C.

α,α Diphenyl - 4,6 - dichloro - 2 - methyl - 5 - pyrimidinemethanol. Melting point: 110—112°C.

### Example 2

5 - Bis(4 - chlorophenyl)methylpyrimidine

A mixture of 6 g. of α,α - bis(4 - chlorophenyl) - 5 - pyrimidinemethanol, 200 ml. of glacial acetic acid, and 10 ml. of 47 percent hydriodic acid was refluxed for 40 minutes, poured into water, and the aqueous mixture extracted several times with ether. The combined ether layers were washed successively with water, 5 percent aqueous sodium bicarbonate solution, and water, dried over anhydrous magnesium sulfate, and evaporated *in vacuo* to dryness. The residue was extracted with petroleum ether and the extracts concentrated. The product was obtained as a thick reddish oil identified by infrared and nuclear magnetic resonance (NMR) spectra as 5 - bis(4 - chlorophenyl)-methylpyridine.

Following the same general procedure as in Example 2, with appropriate starting materials, the following compounds were prepared:

5 - (2 - Fluorodiphenylmethyl)pyrimidine. Melting point: Liquid.

5 - [Bis(3,4 - dichlorophenyl)methyl]pyrimidine. Melting point: Liquid.

### Example 3

α,α - Diphenyl - 5 - pyrimidineacetonitrile

To 0.1 mole of potassium amide in liquid ammonia was added a solution of 0.1 mole of diphenylacetonitrile in 300 ml. of xylene, and the mixture was heated to refluxing for about 30 minutes to remove excess ammonia. To the xylene solution was added a solution of 0.1 mole of 5-bromopyrimidine in 100 ml. of xylene and the mixture stirred for about 20 minutes. To the mixture were then added 20 ml. of dimethylformamide and the mixture was refluxed for about one hour. The reaction product mixture was cooled in an ice bath and extracted with ether. The ether solution was evaporated to dryness, the residue dissolved in benzene and chromatographed on an alumina column, elution being carried out with ethyl acetate. The eluate was concentrated to yield α,α - diphenyl - 5 - pyrimidineacetonitrile as a solid having a melting point of about 98—100°C., identified by NMR spectrum and elemental analysis.

### Example 4

2,4,6 - Trichloro - 5 - phenyl - *p* - tolylmethylpyrimidine

To a solution of 22 g. (0.95 g.-atom) of

sodium in 500 ml. absolute ethanol was added a solution of 33 g. (0.55 mole) of urea and 95 g. (0.28 mole) of ethyl phenyl - *p* - tolylmethyl malonate in 500 ml. of absolute ethanol, and the mixture was refluxed for about two hours. The reaction product mixture was cooled and diluted with about 1000 ml. of water and 500 ml. of ether. The layers were separated. The aqueous layer was washed with about 200 ml. of ether. The ether washings were combined with the original organic layer and washed with 200 ml. water. The washed aqueous layer and the water washings were combined and acidified with concentrated aqueous hydrochloric acid. An oily layer separated which solidified under vacuum. The crude solid was dissolved in dilute aqueous sodium hydroxide and the basic solution acidified with acetic acid. The solid which separated was recrystallized from acetic acid to yield a crystalline solid having a melting point of about 115°C. and identified by NMR spectrum as 5 - (phenyl - *p* - tolylmethyl)barbituric acid. Weight: 45 g.

A mixture of 39 g. (0.13 mole) of 5 - (phenyl - p - tolylmethyl)barbituric acid (prepared above), 116 g. (0.76 mole) of phosphorus oxychloride, and 56 g. (0.38 mole) of N,N-diethylaniline was heated at reflux temperature for about six hours. The reaction product mixture was cooled, diluted with a mixture of crushed ice and water, and allowed to stand for about an hour. The mixture was extracted five times with 300 ml. of ether, the combined extracts were dried, and the solvent was evaporated to dryness on the steam bath. The residue remaining was extracted with hot petroleum ether (b.p.=60—70°C.). The petroleum ether solution was cooled, and a crystalline product separated which had a melting point of about 112—113°C. and weighed about 30 g. It was identified by NMF spectrum and elemental analysis as 2,4,6 - trichloro - 5 - (phenyl - *p* - tolylmethyl)pyrimidine.

Following the general procedure of Example 4, with appropriate starting materials, other compounds were prepared and are listed as follows:

2,4,6 - Trichloro - 5 - (diphenylmethyl)-pyrimide. Melting point: 105—106°C.
2,4,6 - Trichloro - 5 - (phenyl - *p* - anisylmethyl)pyrimidine. Melting point: 129—131°C.
2,4,6 - Trichloro - 5 - (phenyl - *o* - chlorophenylmethyl)pyrimidine. Melting point: 162—163°C.
2,4,6 - Trichloro - 5 - (1 - phenyl - *n* - heptyl)pyrimidine. Melting point: Oil.
2,4,6 - Trichloro - 5 - (1 - phenyl - *n* - tridecyl)pyrimidine. Melting point: Oil.
2,4,6 - Trichloro - 5 - (1 - phenyl - *n* - butyl)pyrimidine. Melting point: 72°C.

EXAMPLE 5

5 - (Phenyl - p - tolylmethyl)pyrimidine)

A mixture of 15 g. (0.041 mole) of 2,4,6 - trichloro - 5 - (phenyl - p - tolylmethyl)-pyrimidine, 12.5 g. (0.124 mole) triethylamine, 100 ml. dry dioxane, and 1 g. of 5 percent palladinized charcoal was hydrogenated on a Paar shaker at an initial pressure of 15 p.s.i. for about 5 hours, during which time the theoretical amount of hydrogen was absorbed. When the hydrogenation was complete, the reaction product mixture was concentrated *in vacuo* to dryness. The residue was dissolved in benzene and chromatographed on an alumina column, eluting with ethyl acetate. A solid was obtained which was recrystallized from petroleum ether to yield crystalline material having a melting point of about 71—72°C., and identified by NMR spectrum and elemental analysis as 5 - (phenyl - p - tolylmethyl)pyrimidine. Weight: 8 g.

Following the general procedure of Example 5 with appropriate starting materials, other compounds were prepared and are listed as follows:

5 - (Diphenylemthyl)pyrimidine. Melting point: 83°C.
5 - Phenyl - *p* - anisylmethyl)pyrimidine. Melting point: Oil.
5 - (Phenyl - *o* - chlorophenylmethyl)-pyrimidine. Melting point: 107—108°C.
5 - (1 - Phenyl - *n* - heptyl)pyrimidine. Melting point: Oil.
5 - (1 - Phenyl - *n* - butyl)pyrimidine. Melting point: Oil.
5 - (1 - Phenyl - *n* - tridecyl)pyrimidine. Melting point: Oil.

EXAMPLE 6

5 - ($\alpha$ - Chlorodiphenylmethyl)pyrimidine

To a refluxing solution of 40 g. of $\alpha,\alpha$ - diphenyl - 5 - pyrimidinemethanol in 200 ml. of xylene was added anhydrous hydrogen chloride gas via a bubbler tube, and the by-product water was collected in a Dean-Stark trap. The reaction product mixture was concentrated in vacuo to dryness. The dry residue was washed with ethyl ether to remove starting material, and ethyl ether-insoluble residue was dissolved in hot petroleum ether. The petroleum ether was evaporated to dryness and the residue recrystallized from ether to yield solid product weighing 6 g. and having a melting point of about 92—94°C. The product was identified as 5 - ($\alpha$ - chlorodiphenylmethyl)pyrimidine by elemental analysis and NMR spectrum.

EXAMPLE 7

5 - ($\alpha,\alpha$ - Diphenyl - $\alpha$ - anilinomethyl)-pyrimidine

A mixture of 5 g. of 5 - ($\alpha$ - chlorodiphenylmethyl)pyrimidine, 10 ml. of aniline,

and 40 ml. of benzene was warmed for about an hour on the steam bath. The reaction product mixture was cooled and filtered to remove aniline hydrochloride, and the filtrate concentrated to dryness. The solid residue was recrystallized from ethyl ether to yield a yellow crystalline product weighing 2 g. and having a melting point of about 140—144°C. The product was identified as 5 - (α,α - diphenyl - α - anilinomethyl)-pyrimidine by NMR spectrum.

EXAMPLE 8

5 - (α,α - Diphenyl - α - hydroxylamino)-pyrimidine

A mixture of 5 g. of 5 - (α - chlorodiphenylmethyl)pyrimidine and excess hydroxylamine in ethanolic sodium ethoxide was refluxed for about one hour. The reaction product mixture was evaporated to dryness and the residue extracted with benzene. The benzene solution was filtered, concentrated to dryness, and the residue extracted with ether. The ether extract was concentrated to dryness, yielding a crude product having a melting point of about 110—125°C., identified by NMR and infrared spectra as 5 - (α,α - diphenyl - α - hydroxylamino)pyrimidine.

EXAMPLE 9

5 - (α - Ethoxydiphenylmethyl)pyrimidine

A mixture of 10 g. of 5 - (α - chlorodiphenylmethyl)pyrimidine and a saturated solution of liquid ammonia in absolute alcohol was prepared and an exothermic reaction took place. When the exothermic reaction had subsided, the reaction product mixture was filtered and the filtrate evaporated to dryness. The solid residue was extracted with chloroform and the chloroform solution allowed to stand overnight at ambient room temperature. The crude crystals which separated were dissolved in ethyl acetate and chromatographed over alumina using a mixture of hexane and ethyl acetate as eluting solvent. A solid having melting point of about 95—97°C. was obtained from the eluate and identified by NMR spectrum and elemental analysis as 5 - (α - ethoxydiphenylmethyl)pyrimidine.

EXAMPLE 10

5 - (α - Aminodiphenylmethyl)pyrimidine

A mixture of 12 g. of 5 - (α - chlorodiphenylmethyl)pyrimidine and an excess of liquid ammonia was heated at a temperature of about 100°C. for about two hours in a closed stainless steel high-pressure reaction vessel. The reaction product was removed from the reaction vessel, the excess ammonia allowed to evaporate, and the residue extracted with benzene. The benzene solution was concentrated to yield a crystalline product having a melting point of about 135—137°C. The product was identified as 5 - (α - aminodiphenylmethyl)pyrimidine by NMF spectrum and elemental analysis.

EXAMPLE 11

5 - [α - (2 - Imidazolylthio)diphenylmethyl]pyrimidine

The potassium salt of 2-mercaptoimidazole was prepared by adding 10 g. of 2-mercaptoimidazole to an ethanol solution of potassium ethoxide prepared from 1 g. of potassium and 200 ml. of absolute ethanol. To the above mixture were added 5 g. of 5 - (α - chlorodiphenylmethyl)pyrimidine and the reaction mixture heated to refluxing for about two hours. The reaction product mixture was concentrated *in vacuo* to dryness and the residue extracted with hot benzene. The benzene extract was cooled, and a solid product crystallized therefrom, weighing 3 g. and having a melting point of about 165—167°C. It was identified as 5 - [α - (2 - imidazolylthio)diphenylmethyl]pyrimidine by elemental analysis and NMR spectrum.

EXAMPLE 12

5 - (α - Phenylphenethyl)pyrimidine

To sodamide in liquid ammonia prepared by the addition of 1.2 g. (0.05 g.-atom) of sodium to 500 ml. of liquid ammonia, were added 8.3 g. (0.05 mole) of 5-benzylpyrimidine, and the resulting red-brown mixture was stirred for about 10 to 15 minutes. A solution of 6.3 g. (0.05 mole) of benzyl chloride in 15 ml. anhydrous ether was added and the reaction mixture stirred about one hour. To the reaction product mixture were added 200 ml. of ether and the mixture were evaporated to near dryness on the steam bath. The residue was slurried again with 200 ml. of ether and evaporated to dryness. The dry residue was dissolved in a mixture of about 500 ml. of ether and 200 ml. of water and the ether layer separated and dried over anhydrous magnesium sulfate. The drying agent was filtered off, and from the ether solution a solid precipitated. The solid, on standing, became an oil, which was dissolved in benzene and chromatographed on an alumina column, elution being carried out with a mixture of ethyl acetate and benzene. From the eluate a solid product was obtained which, upon recrystallization from petroleum ether, had a melting point of about 80—82°C. The crystalline product weighed about 5 g. and was identified as 5 - (α - phenylphenethyl)pyrimidine by elemental analysis and NMR spectrum.

EXAMPLE 13

2 - Methoxy - 5 - (1 - phenyl - *n* - tridecyl)-pyrimidine

4 - Methoxy - 5 - (1 - phenyl - *n* - tridecyl)-pyrimidine

To a mixture of 40 g. (0.09 mole) of 2,4,6 - trichloro - 5 - (1 - phenyl - *n* - tridecyl)-

pyrimidine in a solvent composed of 250 ml. of dry dioxane and 500 ml. of dry methanol were added 8 g. of palladinized charcoal and 15 g. of potassium hydroxide pellets, and the mixture was hydrogenated on a Paar shaker at a pressure of 40 pounds per square inch of hydrogen. The reaction product mixture was filtered to remove catalyst and the filtrate was concentrated to dryness *in vacuo*. The residue was dissolved in a mixture composed of 300 ml. of water and 300 ml. of ethyl ether, the ether layer was separated and dried, and the ether was evaporated to dryness on the steam bath. The residue was dissolved in benzene and chromatographed on an alumina column. Elution was done with a mixture of benzene and ethyl acetate in proportions up to a concentration of about 10 percent ethyl acetate. A total of about 14 g. of an oil was obtained. The oil was dissolved in benzene and placed on a 3-foot alumina column containing about 800 g. of alumina. The material was eluted using a mixed solvent of about 2 percent of ethyl acetate in benzene. The first fractions were concentrated to yield 3.5 g. of product, identified by NMR spectrum as 2 - methoxy - 5 - (1 - phenyl - n - tridecyl)pyrimidine.

The next fractions, totaling 4.0 g. on concentration to dryness, were combined, shown by NMR spectrum to be an undesirable mixture and discarded. The last fractions, weighing 5.5 g. were obtained using an eluting solvent of 10 percent ethyl acetate in benzene, and were identified by NMR spectrum as 4 - methoxy - 5 - (1 - phenyl - *n* - tridecyl)-pyrimidine.

### Example 14

5 - ($\alpha$ - Acetaminodiphenylmethyl)pyrimidine

A mixture of 4.5 g. of 5 - ($\alpha$ - aminodiphenylmethyl)pyrimidine and 50 ml. of acetic anhydride was heated until a homogeneous solution was obtained. The reaction product mixture was allowed to stand at ambient room temperature overnight and then was concentrated *in vacuo* to remove the solvent, leaving a dry residue. The residue was recrystallized from hot benzene to yield about 2.5 g. of crystalline product having a melting point of about 187—189°C. The product was identified as 5 - ($\alpha$ - acetaminodiphenylmethyl)pyrimidine by elemental analyses and NMR spectrum.

### Example 15

$\alpha$ - (4 - Fluorophenyl) - $\alpha$ - phenyl - 5 - pyrimidinemethanol

To 300 ml. of anhydrous ether maintained in an atmosphere of dry nitrogen gas in a suitably equipped 3-neck round-bottom reaction flask cooled to −118°C. by an alcohol-liquid nitrogen cooling bath, were added 170 ml. (0.3 mole) of a 15 percent solution of butyl lithium in hexane. Cooling and stirring and the dry nitrogen atmosphere were continued while a solution of 0.3 mole of 5-bromopyrimidine in 150 ml. of dry tetrahydrofuran was added and the whole stirred for about two hours. The temperature of the reaction mixture was lowered to −125° C. and a solution of 0.3 mole of 4-fluorobenzophenone in 150 ml. of dry tetrahydrofuran was added slowly while maintaining the temperature of the mixture at about −120°C. The reaction product mixture was stirred overnight and warmed to ambient room temperature. The reaction product mixture was neutralized by the addition of a saturated aqueous solution of ammonium chloride. The neutralized mixture was extracted with ether and the combined ether extracts dried over anhydrous potassium carbonate, filtered, and concentrated to dryness *in vacuo* and the residue dissolved in benzene. The benzene solution was chromatographed over 1500 g. of silica gel, elution being accomplished with an ethyl acetate-benzene mixture, using a gradient elution technique. The fraction obtained using a solvent containing 30:50 ethyl acetate-benzene was concentrated to dryness at reduced pressure, yielding 52 g. of product having a melting point of about 112—114°C. after recrystallization from ether. The product was identified by elemental analyses and NMR spectrum as $\alpha$ - (4 - fluorophenyl) - $\alpha$ - phenyl - 5 - pyrimidinemethanol.

### Example 16

2 - Methyl - 4,6 - dichloro - 5 - (diphenylmethyl)pyrimidine

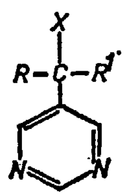
A mixture of 16 g. of sodium methoxide, 28 g. of ethyl diphenylmethyl malonate, and 9.5 g. of acetamidine hydrochloride in 250 ml. of anhydrous methanol was stirred and refluxed for about six hours. The reaction product mixture was evaporated to dryness *in vacuo*, the residue dissolved about one liter of water and the mixture acidified with concentrated aqueous hydrochloric acid, whereby a white solid precipitated. The solid was filtered off and recrystallized from boiling ammonium hydroxide, the product crystallizing as the excess ammonia evaporates. The solid product was filtered off and dried by slurrying in boiling benzene to yield 17 g. of product having a melting point of about 355°C. (dec.) and identified by its NMR spectrum as 2 - methyl - 4,6 - dihydroxy - 5 - (diphenylmethyl)pyrimidine.

A mixture of 12 g. of 2 - methyl - 4,6 - dihydroxy - 5 - (diphenylmethyl)pyrimidine and 300 ml. of phosphorous oxychloride was refluxed for about one hour. The reaction product mixture was concentrated at reduced pressure to remove excess phosphorous oxychloride, poured into a mixture of crushed ice and water, and extracted several times with ethyl ether. The ether extracts were

concentrated to yield 11 g. of product having a melting point of about 112—115°C. and identified by NMR spectrum as 2 - methyl - 4,6 - dichloro - 5 - (diphenylmethyl)pyrimidine.

WHAT WE CLAIM IS:—

1. A pyrimidine compound of the formula:



wherein

R is $C_1$—$C_{13}$ alkyl, $C_3$—$C_4$ cycloalkyl, or phenyl;

$R^1$ is benzyl, phenyl, thienyl, or furyl, $C_1$—$C_{13}$ alkyl, or $C_3$—$C_4$ cycloalkyl;

X is hydrogen, hydroxyl, $C_1$—$C_4$ acyloxy, halo, amino, ($C_1$—$C_4$ acyl) amino, $C_1$—$C_3$ alkyl, cyano, $C_1$—$C_3$ alkoxy, $C_1$—$C_4$ alkylmercapto, heterocyclic-mercapto, anilino, or hydroxylamino; and wherein R, $R^1$, X and the pyrimidine ring may be substituted by one or more of the radicals, chloro, bromo, fluoro, iodo, trifluoromethyl, hydroxy, methyl, ethyl, methoxy, methylmercapto, methylsulfonyl, nitro or dialkylamino; or a non-phytotoxic acid addition salts thereof; and excluding 5-isopropylpyrimidine and 5-isoheptylpyrimidine.

2. The pyrimidine compound of claim 1 being 5 - (diphenylmethyl)pyrimidine; α - (2 - chlorophenyl) - α - (3 - chlorophenyl) - 5 - pyrimidinemethanol; α - (2 - fluorophenyl - α - (3 - fluorophenyl) - 5 - pyrimidinemethanol; α,α - diphenyl - 5 - pyrimidineacetonitrile or α - (4 - fluorophenyl) - α - phenyl - 5 - pyrimidinemethanol.

3. A pyrimidine compound of claim 1 as herein described with particular reference to the examples.

4. A fungicidal composition when comprising a compound as claimed in any one of claims 1 to 3 and a fungicidal carrier.

5. A fertiliser composition when comprising a compound as claimed in any one of claims 1 to 3 and one or more plant foods.

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